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Bureau voor de Industriële Eigendom

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This is to declare that in the Netherlands on July 9, 2003 under No. PCT/NL 03/00503,
in the name of:

DSM IP ASSETS B.V.

in Heerlen, the Netherlands and

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in Landgraaf, the Netherlands and

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in Sittard, the Netherlands

an international patent application was filed for:

"Process for the production of a polymer comprising monomeric units of ethylene, an a-olefin and a vinyl norbornene",

and that the documents attached hereto correspond with the originally filed documents.

Rijswijk, July 15, 2004.

In the name of the president of the Netherlands Industrial Property Office

Mrs. D.L.M. Brouwer

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SUBMITTED OR TRANSMITTED IN
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PROCESS FOR THE PRODUCTION OF A POLYMER COMPRISING MONOMERIC UNITS OF ETHYLENE, AN A-OLEFIN AND A VINYL NORBORNENE

The invention relates to a process for the preparation of a polymer comprising monomeric units of ethylene, an α-olefin and a vinyl norbornene. The invention also relates to a polymer obtainable by the process of the invention.

Such a process and polymer are known from EP-A-765908. In this patent application a polymer consisting of ethylene, propylene and vinyl norbornene is described as well as various processes for the production the polymer. An advantage of the polymer comprising the monomeric units of vinyl norbornene is that it cures fast and to a high level when using a peroxide as a curative. For that reason it is desirable to use the polymer in rubber composition suitable for peroxide curing, like for instance rubber compositions used for the production of cable and wire, hoses for automotive applications, like for instance radiator hoses and hoses used in the braking system, thermoplastic elastomers and a wide variety of further rubber applications.

A serious disadvantage however is that in the production of the polymer comprising the vinyl norbornene using one of the known processes is that a high amount of branches is formed in the polymer and sometimes even gelation of the polymer takes place. Due to the high amount of branches the polymer has a broad molecular weight distribution. This is a disadvantage for the mechanical properties of a rubber comprising the polymer. If gelation occurs the polymer is partly or entirely cross-linked. The gelation is disadvantageous, as it causes the polymerization process to be unstable, reactor fouling to take place and the polymer to be not useful for use in a rubber composition intended for the production of shaped articles.

Object of the invention is to provide a process for the preparation of a polymer comprising monomeric units of ethylene, an α-olefin and a vinyl norbornene, the polymer showing less branches and no or at least decreased gelation.

Surprisingly such a process is obtained, because the polymer is prepared by using a catalyst system comprising as components:

a. bridged or an unbridged group 4 metal containing catalyst having a single cyclopentadienyl ligand, a nitrogen containing ligand and at least one activatable ligand.

b. an aluminoxane activating compound,

c. 0 - 0.20 mol per mol of the catalyst of a further activating compound.

Preferably in the process according to the invention a bridged or an unbridged catalyst is used according to formula:

$$\begin{array}{ll} \text{Cp} & \\ \vdots & \backslash \\ \vdots & \text{M -Xn} \\ \vdots & / \\ \text{Z} & \end{array}$$

Form. I

wherein Cp is a ligand selected from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl and substituted fluorenyl;

X is an activatable ligand

Z is a nitrogen containing ligand

n is 1 or 2.

More preferably as a catalyst is used:

an unbridged catalyst having a single cyclopentadienyl ligand and a mono substituted nitrogen ligand, wherein said catalyst is defined by the formula:

$$\begin{array}{l} \text{Cp} \\ \quad \backslash \\ \quad \text{M} - \text{Xn} \\ \quad / \\ \text{N} \\ \| \\ \text{Y} \end{array}$$

Form. II

wherein Y is selected from the group consisting of:

ai) a phosphorus substituent defined by the formula:

$$\begin{array}{l} \quad R^1 \\ \quad / \\ P - R^1 \\ \quad \backslash \\ \quad R^1 \end{array}$$

Form. III

wherein each R^1 is independently selected from the group consisting of a hydrogen atom, a halogen atom, C_{1-20} hydrocarbyl radicals which are unsubstituted by or

further substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical of the formula:

$$-Si-(R^2)_3 \qquad \text{Form. IV}$$

wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, and a germanyl radical of the formula:

$$-Ge-(R^{2'})_3 \qquad \text{Form. V}$$

wherein $R^{2'}$ is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals,

aii) a substituent defined by the formula:

```
      Zm
     /  \
  Y'n    Y'k
   |      |                 Form. VI
 R3-N    N-R3
     \  /
      C
```

wherein each of Y is $C R^3 R^3$, $C=C R^3 R^3$, $C=N R^3$, SiRR, C=O, $N R^3$, $P R^3$, O or S,

Z is - A=A-, and each A is $C R^3$, N or P,

each R^3 is independently selected from the group of hydrogen, hydrocarbyl radical, silyl radical according to form. III or germanyl radical according to form. IV,

k, m and n have independently the value 0, 1, 2 or 3, provided that $k + m + n > 0$, and

aiii) a substituent defined by the formula:

```
  Sub1
  /
 C
  \
  Sub2            Form. VII
```

wherein each of Sub^1 and Sub^2 is independently selected from the group consisting of hydrocarbyls having from 1 to 20 carbon atoms; silyl groups, amido groups and phosphido groups,

Cp is a ligand selected from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl and substituted fluorenyl;
X is an activatable ligand and n is 1 or 2, depending upon the valence of M and the valence of X; and
M is a group 4 metal selected from the group consisting of titanium, hafnium and zirconium.

Surprisingly with the process according to the invention the polymer comprising the monomeric units of ethylene, the α-olefin and the vinyl norbornene shows considerable less long chain branching and no or hardly any gelation. A further advantage is that in the polymer obtained with the process according to the invention a larger portion of the vinyl norbornene is polymerized with only one of the two double bonds, the second double bond being available for the curing of the polymer. This results in a polymer being even more reactive to peroxide curing.

A process for the preparation of a polymer comprising monomeric units of ethylene, an α-olefin and non-conjugated diene, while using the above defined catalyst is described in EP-A-1162214. However in the document it is disadvised to use alominoxane as an activating compound and no attention is paid to the specific preparation of a polymer comprising vinyl norbornene.

Preferably 0 - 0.1 mol per mol of catalyst of further activating compound is used. Most preferably no further activating compound is used at all. In that case the aluminoxane is used as the sole activating compound.

The catalyst used in the process according to the invention preferably contains a phosphinimine ligand which is covalently bonded to the metal. This ligand is defined by the formula:

$$\begin{array}{c} R^1 \\ \quad\backslash \\ R^1 - P{=}N - \\ \quad / \\ R^1 \end{array} \qquad \text{Form. VIII}$$

wherein each R^1 is independently selected from the group consisting of a hydrogen atom, a halogen atom, C_{1-20} hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical,

an amido radical, a silyl radical of the formula:

$$-Si-(R^2)_3 \qquad \text{Form. IV}$$

wherein each R is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, and a germanyl radical of the formula:

$$-Ge-(R^{2'})_3 \qquad \text{Form. V}$$

wherein $R^{2'}$ is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals.

This ligand contains a "mono substituted nitrogen atom" in the sense that there is only one phosphorus atom (doubly) bonded to the nitrogen atom.

The preferred phosphinimines are those in which each R' is a hydrocarbyl radical. A particularly preferred phosphinimine is tri-(tertiary butyl) phosphinimine (i.e. where each R' is a tertiary butyl group).

As used herein, the term "ketimide ligand" refers to a ligand which: (a) is bonded to the transition metal via a metal-nitrogen atom bond; (b) has a single substituent on the nitrogen atom, (where this single substituent is a carbon atom which is doubly bonded to the N atom); and (c) preferably has two substituents (Sub 1 and Sub 2, described below) which are bonded to the carbon atom.

Conditions a, b and c are illustrated below:

```
Sub 1     Sub 2
    \     /
       C
       ||          Form. IX
       N
       |
     metal
```

This ligand also contains a mono substituted nitrogen atom in the sense that only one carbon atom is (doubly) bonded to the nitrogen atom.

The substituents "Sub 1" and "Sub 2" may be the same or different. Exemplary substituents include hydrocarbyls having from 1 to 20 carbon atoms; silyl groups, amido groups and phosphido groups.

As used herein, the term cyclopentadienyl ligand is meant to broadly

convey its conventional meaning, namely a ligand having a five carbon ring which is bonded to the metal via eta-5 bonding. Thus, the term "cyclopentadienyl" includes unsubstituted cyclopentadienyl, substituted cyclopentadienyl, unsubstituted indenyl, substituted indenyl, unsubstituted fluorenyl and substituted fluorenyl. An exemplary list of substituents for a cyclopentadienyl ligand includes the group consisting of C_{1-10} hydrocarbyl radical (which hydrocarbyl substituents are unsubstituted or further substituted); a halogen atom, C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical; an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; silyl radicals of the formula:

$$-Si-(R^2)_3 \qquad \text{Form. IV}$$

wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical C6-10 aryl or aryloxy radicals; germanyl radicals of the formula:

$$-Ge-(R^{2'})_3 \qquad \text{Form. V}$$

wherein $R^{2'}$ is as defined directly above.

The catalyst used in the process of this invention must also contain an activatable ligand. The term "activatable ligand" refers to a ligand which may be activated by the aluminoxane activating compound (or the aluminoxane compound and eventually a minor portion of a further activating compound to facilitate olefin polymerization). Exemplary activatable ligands are independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-10} hydrocarbyl radical, a C_{1-10} alkoxy radical, a C_{5-10} aryl oxide radical; each of which said hydrocarbyl, alkoxy, and aryl oxide radicals may be unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, a Silicium radical, an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals.

The number of activatable ligands depends upon the valency of the metal and the valency of the activatable ligand. The preferred catalyst metals are Group 4 metals in their highest oxidation state (i.e. 4+) and the preferred activatable ligands are monoanionic (such as a hydrocarbyl group - especially methyl). Thus, the preferred catalyst contain a phosphinimine ligand, a cyclopentadienyl ligand and two chloride (or methyl) ligands bonded to the Group 4 metal. In some instances, the metal of the catalyst

component may not be in the highest oxidation state. For example, a titanium (III) component would contain only one activatable ligand, if Z is anionic.

The most preferred catalysts for use in the process according to the invention are Group 4 organometallic complex in its highest oxidation state having a phosphinimine ligand, a cyclopentadienyl-type ligand and two activatable ligands. These requirements may be concisely described using the following formula for the preferred catalyst:

$$\begin{array}{c} \mathrm{Pl} \\ | \\ \mathrm{Cp} - \mathrm{M} - (\mathrm{X})_2 \end{array} \qquad \text{Form. X}$$

wherein: (a) M is a metal selected from Ti, Hf and Zr; (b) Pl is the phosphinimine ligand according to Form. VI as defined above. (c) Cp is a ligand selected from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl, substituted fluorenyl; and (d) X is an activatable ligand.

Although it is well known that aluminoxanes may be used as co catalysts and/or as a catalyst poison scavenger and/or as an alkylating agent, aluminoxane nowadays is not preferred any more to be used. Most often the aluminoxane is a mixture of different organo aluminum compounds.

The alumoxane may be of the overall formula: $(R^4)_2AlO(R^4AlO)_mAl(R^4)_2$ wherein each R^4 is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and m is from 0 to 50, preferably R^4 is a C_{1-4} radical and m is from 5 to 30. Methylalumoxane (or "MAO") in which most of the R groups in the compounds of the mixture are methyl is the preferred alumoxane.

Alumoxanes are also readily available articles of commerce generally as a solution in a hydrocarbon solvent.

The alumoxane, when employed, is preferably added at an aluminum to transition metal (in the catalyst) mole ratio of from 20:1 to 1000:1. Preferred ratios are from 50:1 to 250:1.

It is preferred to use a sterically bulky compound to enhance catalyst activity in the process of the present invention. Sterically bulky amines and/or sterically bulky alcohols are preferred. Hindered phenols are most preferred.

The process of the present invention may be a bulk polymerization

process, a solution polymerization process or a slurry polymerization process.

The process of the present invention preferably is a solution process. Solution processes for the polymerization of ethylene propylene elastomers are well known in the art. These processes are conducted in the presence of an inert hydrocarbon solvent such as a C_{5-12} hydrocarbon which may be unsubstituted or substituted by a C_{1-4} alkyl group such as pentane, methyl pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane and hydrogenated naphtha.

The process of this invention may be undertaken at a temperature of from 20 DEG C to 150 DEG C. As previously noted, the use of a higher polymerization temperature will generally reduce solution viscosity (which is desirable) but also reduce molecular weight (which may be undesirable).

The monomers used in the process according to the invention for the preparation of the polymer may be dissolved/dispersed in the solvent either prior to being fed to the reactor (or for gaseous monomers the monomer may be fed to the reactor so that it will dissolve in the reaction mixture). Prior to mixing, the solvent and monomers are preferably purified to remove potential catalyst poisons such as water or oxygen. The feedstock purification follows standard practices in the art, e.g. molecular sieves, alumina beds and oxygen removal catalysts are used for the purification of monomers. The solvent itself as well (e.g. methyl pentane, cyclohexane, hexane or toluene) is preferably treated in a similar manner.

The feedstock may be heated or cooled prior to feeding to the polymerization reactor. Additional monomers and solvent may be added to a second reactor (if employed) and the reactor(s) may be heated or cooled.

Generally, the catalyst components may be added as a separate solutions to the reactor or premixed before adding to the reactor.

The residence time in the polymerization reactor will depend on the design and the capacity of the reactor. Generally the reactors should be operated under conditions to achieve a thorough mixing of the reactants. If two reactors in series are used, it is preferred that from 50 to 95 weight % of the final polymer is polymerized in the first reactor, with the balance being polymerized in the second reactor. It is also possible to use a dual parallel reactor setup. On leaving the reactor the solvent is removed and the resulting polymer is finished in a conventional manner.

It is also within the scope of this invention to use more than two polymerization reactors.

The invention also relates to the polymer obtainable by the process according to the invention. The invention also relates to compounds comprising the polymer obtainable by the process of the present invention, a plasticizer and a filler.

Due to the relatively high fraction of the vinyl norbornene non-conjugated diolefins that is polymerized with only one of the double bonds, the polymer comprises a lot of double bonds originating from the vinyl norbornene available for curing. It is known that the double bonds originating from the vinyl norbornene give a high curing speed, especially if a peroxide based curing system is used.

For these reasons it is very desirable to use the polymer of the present invention for the production in peroxide curing processes, preferably for the production of hoses, cable and wire covering, profiles and thermoplastic vulcanizates.

The polymer obtainable with the process of the present invention may contain monomeric units of one or more α-olefins having from 3 to for example 23 carbon atoms. Examples of such α-olefins are propylene, 1-butene, 1-pentene, 1-hexene and 1-octene. Preferably the polymer contains monomeric units of propylene as the α-olefin.

The polymers may have a weight average molecular weight of 10000 to 500000 kg/kmol. Preferably, the polymers have a weight average molecular weight of 20000 to 400000 kg/kmol, more preferably 50000 to 300000 kg/kmol.

The polymer for example contains 0.01 - 20 weight % vinyl norbornene, preferably 0.1 - 10 weight % mol.%, more preferably 0.2 - 6 weight %.

The preferred vinyl norbornene is 5-vinyl-2-norbornene. In one embodiment of the invention the polymer exists of ethylene, the α-olefin and the vinyl norbornene. In a second embodiment of the invention the polymer comprises ethylene, the α-olefin, the vinyl norbornene and a further non-conjugated diene, for example dicyclopentadiene, 1,4-hexadiene, 5-methylene-2-norbornene and 5-ethylidene-2-norbornene, preferably 5-ethylidene-2-norbornene.

Preferably the polymer comprises at least 0.01 weight % 5-ethylene-2-norbornene, more preferably at least 0.05 weight %.

Preferably the polymer comprises from 40 to 90 weight % of ethylene, from 0.1 to 10 weight % of the non-conjugated dienes, the balance being the α-olefin.

Very good results are obtained if the polymer fulfills the following conditions:

[VNB] > 0.01 and

$\Delta\delta > 30 - 15[VNB]$, provided that $\Delta\delta$ has no value below 0, whereby

[VNB] is the content of vinyl norbornene in the polymer in weight % and

$\Delta\delta$ is, expressed in degrees, the difference between the loss angle δ at a frequency of 0.1 rad/s and the loss angle δ at a frequency of 100 rad/s, whereby the loss angle is calculated from the formulae $tg\delta = G''/G'$, whereby G' is the storage modulus and G" is the loss modulus, as measured by RDA (Rheometric ™Dynamic Analyser) at a temperature of 125°C.

More preferably $\Delta\delta > 35 - 15[VNB]$.

Most preferably next to above conditions the polymer fulfills also the following condition:

$\Delta\delta > 25 - 12{,}5.(Q^{-2})$,

wherein Q = Mw/Mn, Mw is the weight average molecular weight and Mn is the number average molecular weight.

Below, the invention will be elucidated on the basis of the following examples and comparative experiments, without being limited thereto.

ANALYSIS OF THE ELASTOMERIC COPOLYMERS.

Mw and Mn, weight and number average molecular weight.

The elastomeric copolymers that were prepared as described in the examples were analyzed by means of Size Exclusion Chromatography and Differential Viscosimetry (SEC-DV) in accordance with the method described in the foregoing. All copolymers were elastomeric and in a DSC analysis they showed no peaks with a peak temperature higher than 25°C.

The equipement and the experimental conditions for this SEC-DV analysis were as follows:

Equipment:	Waters M150c Gel Permeation Chromatograph (GPC) with DRI detector, used for Size Exclusion chromatography

	Viscotek Differential Viscometer (DV), model 100-02
	Detectors in parallel configuration with heated line interface (HLI)
	Erma solvent degasser ERC-3522
	LiChroma III pump pulse dampener (Viscotek) and high-sensitivity accessory (Waters)
Data processing:	Viscotek data processing software, UNICAL 4.04 or higher version
Columns:	Toyo Soda (TSK) GMHXL-HT mixed bed (4x)
Calibration:	Universal calibration with linear polyethylene (PE) standard (molecular weight 0.4-4000 kg/mol)
Temperatures:	Column oven 140°C
	Injector compartment 150°C
	Pump solvent compartment 60°C
	DV oven 150°C
SEC conditions:	Flow: 1.0 ml/min
Injection volume:	0.300 ml
Solvent/eluent:	Distilled 1,2,4-trichlorobenzene with about 1 g/l of Ionol stabilizer
Sample preparation:	Dissolving for 4 hours at approx. 150°C
	Filtration through 1.2 micron Ag filter
	Sample concentration approx. 1.0 mg/ml

Composition of the polymers.

By means of Fourier transformation infrared spectroscopy (FT-IR), the composition of the copolymers was determined according to the method that is customary in the rubber industry. The FT-IR measurement gives the composition of the various monomers in weight per cents relative to the total composition.

$\Delta\delta$.

$\Delta\delta$ is, expressed in degrees, the difference between the loss angle δ at a frequency of 0.1 rad/s and the loss angle δ at a frequency of 100 rad/s. The loss angle is calculated from the formulae $tg\delta = G''/G'$, whereby G' is the storage modulus and G" is the loss modulus, as measured by RDA (Rheometrics™ Dynamical Analyser) at a temperature of 125 °C.

ML(1+4) 125 °C.

Mooney viscosity, measured at 125 °C.

CONTINUOUS POLYMERISATION PROCEDURE.

The polymerization was carried out in one or two solution polymerization reactors (with a volume of 3L each). The feed streams were purified by contacting with various absorption media to remove catalyst killing impurities such as water, oxygen and polar compounds as is known to those skilled in the art.

The process is continuous in all feed streams. Premixed hexane, propene, ethylene, dienes, hydrogen, aluminoxane and the sterically bulky amines and/or sterically bulky alcohols were precooled before being fed to the (first) reactor. The precatalyst and if applicable t-BF20 borate solution were fed separately to the (first) reactor. The polymer solution was continuously removed through a discharge line and worked-up by continuously steam stripping and subsequently a batch wise drying the polymer produced during a well-defined time on a mill.

The conditions and polymer data are presented in tables 2 and 3.

Table 1: Explanation of catalyst components.

Cat 1	Catalyst, η^5-(perfluorophenylcyclopentadienyl)(tri-*tert*-butylphosphinimine) titanium dichloride.
Cat 2	Catalyst, η^5-(perfluorophenylcyclopentadienyl)(tri-*tert*-butylphosphinimine) titanium dimethyl.
Cat 3	Catalyst, η^5-(cyclopentadienyl)(tri-*iso*-propylphosphanimine) titanium dimethyl.
MMAO-7	Modified methylaluminoxane purchased from AKZO-Nobel, the Netherlands. Typical Al content: 13.7 wt% in Isopar E.
PMAO-IP	Poly methylaluminoxane – improved performance purchased from AKZO-Nobel, the Netherlands. Typical Al content: 13.4 wt% in toluene.
BHT	2,6-di-*tert*-butyl-4-methylphenol.
BHEB	2,6-di-*tert*-butyl-4-ethylphenol.
t-BF_{20}	trytilium tetrakis (perfluorophenyl) borate
CGC	Constrained Geometry Catalyst $Me_2SiC_5Me_4$(N-t-Bu)$TiMe_2$
SEAC	Ethylaluminium sesquichloride
dcpae	Dichlorophenyl acetic ethyl ester

From the data in the tables it is clear that in the case of the examples according to the present invention more VNB can be incorporated for equal $\Delta\delta$ compared

to the comparative examples that used a "high" amount of t-BF20 cocatalyst.

A (very) lower $\Delta\delta$ value is indicative of the presence of more (highly) branched polymer material. Gel formation is related to the presence of more, highly branched material.

Example 1 versus Comparative experiment A.

In example 1 the catalyst has been applied with MMAO-7 as catalyst activator. The produced EPDM polymer needed a high VNB content to obtain a reasonably degree of branching, in terms of $\Delta\delta$ of 18.5. The polymer of comparative experiment A, were BF20 had been applied as catalyst activator, under further similar conditions, had a significant lower VNB content whereas the degree of branching was higher resulting in a lower $\Delta\delta$ (12.1).

Examples 1 and 2 versus Comparative experiments A and B.

2) The phenomenon is independent of the reactor set up. In examples 1 and 2 MMAO-7 was used as catalyst activator. Example 1 had a single reactor set up (3 L), while example 2 had a two reactor set up in series (3 L + 3 L). In these experiments for both EPDM polymers had a high VNB content at a moderate degree of branching ($\Delta\delta$ of 18.5 and 15.5). In comparative experiments A and B BF20 was used as catalyst activator. Comparative experiment A had a one reactor set up (3 L), while comparative experiment B had a two reactor set up in series (3 L + 3 L). In both experiments EPDM polymers were produced with low VNB content, resulting in a higher degree of branching (both with $\Delta\delta$ of 12.1).

Example 3.

In example 3i an EPDM polymer was produced with an extreme high VNB content (4wt%). The applied catalyst activator was MAO.

Example 4 versus comparative experiment D

4) In example 4 a EPDM polymer with very high VNB content (3.2) was produced with a MAO activated catalyst. In comparative experiment D a borate activated catalyst was used under further the same conditions. Compared to comparative

experiment D the VNB-content in Example 4 was approximately ten times as high to obtain an equal amount of branching, in terms of $\Delta\delta$ (iv : 9.0 and d : 8.6).

Examples 5, 7 and 8.

In examples 5 and 7 two different catalysts according to the invention were used and an activated MAO. In example 5 (Cat3) the VNB content is higher while only a moderate degree of branching was obtained ($\Delta\delta$ of 20). In example 8 (Cat1) the VNB content was low and only less branching was obtained ($\Delta\delta$ of 30).

Example 8 versus comparative experiment D.

In example 8 (MAO activated) and comparative experiment D (borate activated) two EPDM polymers were produced with equal VNB content (0.32 wt% and 0.34 wt%). In both cases catalyst 1 had been applied. The MAO activated example 8 was hardly branched ($\Delta\delta$ of 30), while the borate activated comparative example D was highly branched ($\Delta\delta$ of 8.6).

Example 6.

7) In example 6 BHEB was used instead of BHT. Also in this case, the VNB content can be high without a too high degree of branching.

Example 7 versus comparative experiment A.

8) In example 7 (MAO activated) no BEHB or BHT has been used. The polymer was hardly branched ($\Delta\delta$ of 34). In comparative experiment A (borate activated) an EPDM polymer with the same VNB content was produced (0.29 wt%), having a considerably amount of branching ($\Delta\delta$ of 12.1).

Example 9.

In example 9 MMAO-7 was used. The produced EPDM polymer had a low VNB content, resulting in a low degree of branching, in terms of $\Delta\delta$ of 34.4.

Comparative experiment F.

In comparative experiment F efforts were made to produce an EPDM polymer having a high VNB content applying a borate activated catalyst. It was not possible to run such experiment under stable conditions without to much reactor fouling.

Table 2: Polymerisation conditions

Example	C6 l/h	C2 NL/h	C3 g/h	ENB mmol/L C6	VNB mmol/L C6	MMAO-7 mmol/h	BHT mmol/h	BHEB mmol/h	CoCat t-BF20 mmol/h	Cat	Cat mmol/h	Temp °C (1st reactor)	Temp °C (2nd reactor)	Prod rate g/h
1	18	905	1058	18.9	9.4	10.4	5.2	-		2	0.057	90	-	1475
2	16.6	1119	1832	26.7	22.2	8.7	4.4	-		2	0.012	91	89	1710
3	17.3	1048	1511	5.1	50.8	11	5.5	-		2	0.046	90	-	1478
4	16.5	1001	2031	5.3	41.7	10.4	5.2	-		2	0.029	89	-	1462
5	14.5	992	3313	66.5	19.9	6.18	11	-		2	0.070	93	-	1930
6	17.3	1106	1596	27.6	18.6	4.3	-	4.14		2	0.051	90	-	1979
7	17.2	1138	1349	20.3	3.4	3.6	-	-		2	0.046	94	-	1763
8	18.1	1123	900	19.3	2.9	18.3	4.8	-		1	0.546	89	-	1408
9	18.1	1125	899	19.0	3.8	7.87	3.99	-	-	2	0.013	89.7	-	1500

Example	C6 l/h	C2 NL/h	C3 g/h	ENB mmol/L C6	VNB mmol/L C6	MMAO-7 mmol/h	BHT mmol/h	BHEB mmol/h	CoCat t-BF20 mmol/h	Cat	Cat mmol/h	Temp °C (1st reactor)	Temp °C (2nd reactor)	Prod rate g/h
Comparative experiments														
A	18	897	1136	19.1	2.8	3.28	1.64	-	0.01	2	0.007	91	-	1476
B	18	844	1132	17.4	2.6	3.28	1.6		0.03	2	0.010	89	81	1478
C	18.1	1139	836	19.2	3.8	3.94	1.87		0.02	1	0.008	91.6	-	1516
D	15.1	855	3180	24.2	8.1	-	-		-	V cat system*		50.6	-	1247
E	18.0	969	523	32.3	-	4.34	2.16		0.039	CGC	0.026	82.2	-	1419
F	Attempt to run a polymerisation process													

* Vanadium based Ziegler Natta cat system consisted of 1.63 SEAC mmol/l C6, 0.055 mmol/lC6 $VOCl_3$ and 0.22 mmol/lC6 DCPAE

Table 3 polymer characterisation data

Example	Wt% C2	Wt% ENB	Wt% VNB*	ML(1+4) 125°C	MSR	Mw Kg/mol	Mw/Mn	Mz/Mw	Δδ			
1	65.9	2.54	1.12	68	0.53	260	3.2	3.4	18.5			
2	67.3	2.34	1.65	66	0.55	245	2.9	3.1	15.5			
3	67.6	0.59	4.04	59	0.43	280	4.5	5.0	1.5			
4	62.8	0.57	3.22	28	0.55	215	3.9	5.3	9.0			
5	54.6	5.29	1.33	78	0.50	280	3.0	3.3	20.0			
6	65.0	2.32	1.42	63	0.52	240	3.7	3.8	13.4			
7	72.6	2.19	0.28	64	1.05	190	2.2	2.1	45.3			
8	67.3	2.46	0.32	60	0.85	210	2.4	2.2	29.6			
9	69.8	2.26	0.40	63	0.90	205	2.1	2.1	34.4			
Comparative experiments												
A	66.7	2.51	0.29	64	0.57	230	2.6	2.5	12.1			
B	61.8	2.40	0.29	60	0.55	215	2.6	2.5	12.1			
C	66.9	2.15	0.34	60	0.44	260	5.9	3.2	8.6			
D	65.7	2.43	0.58	66	0.58	225	2.5	2.3	13.6			
E	66.3	2.83	-	60	0.58	190	2.4	1.9	7.9			
F	It was not possible to run an experiment at high VNB feed using t-BF20 as activator in an appropriate way. Even during the start up, the experiment failed, due to fouling by gelation.											

*: [VNB] as single incorporated VNB , measured with FT-IR

CLAIMS.

1. Process for the preparation of a polymer comprising monomeric units of ethylene, an α-olefin and a vinyl norbornene applying as a catalyst system:

   a. a bridged or an unbridged group 4 metal containing catalyst having a single cyclopentadienyl ligand, a nitrogen containing ligand and at least one activatable ligand.

   b. an aluminoxane activating compound,

   c. 0 - 0.20 mol per mol of the catalyst of a further activating compound.

2. Process according to claim 1, wherein a bridged or unbridged catalyst is used according to formula:

$$\begin{array}{lll} Cp & & \\ \vdots & \backslash & \\ \vdots & M\text{-}X_n & \\ \vdots & / & \\ Z & & \end{array} \qquad \text{Form. I.}$$

   wherein Cp is a ligand selected from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl and substituted fluorenyl;

   X is an activatable ligand

   Z is a nitrogen containing ligand

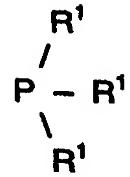
   n is 1 or 2.

3. Process according to claim 1, wherein as unbridged catalyst having a single cyclopentadienyl ligand and a substituted nitrogen ligand, a catalyst is used defined by the formula:

$$\begin{array}{ll} Cp & \\ \ \backslash & \\ \ \ M & - X_n \\ \ / & \\ N & \\ \| & \\ Y & \end{array} \qquad \text{Form. II.}$$

   wherein Y is selected from the group consisting of:

   ai) a phosphorus substituent defined by the formula:



Form. III.

wherein each R^1 is independently selected from the group consisting of a hydrogen atom, a halogen atom, C_{1-20} hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical of the formula:

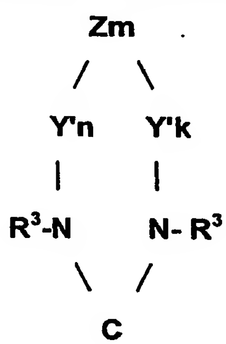
$$-Si-(R^2)_3 \qquad \text{Form. IV.}$$

wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, and a germanyl radical of the formula:

$$-Ge-(R^{2'})_3 \qquad \text{Form. V.}$$

wherein $R^{2'}$ is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals,

aii) a substituent defined by the formula:



Form. VI.

wherein each of Y is C R^3 R^3, C=C R^3 R^3, C=N R^3, SiRR, C=O, N R^3, P R^3, O or S,

Z is - A=A-, and each A is C R^3, N or P,

each R^3 is independently selected from the group of hydrogen, hydrocarbyl radical, silyl radical according to form. III or germanyl radical according to form. IV,

k, m and n have independently the value 0, 1, 2 or 3, provided that $k + m + n > 0$ and

aiii) a substituent defined by the formula:

$$\begin{array}{l} Sub^1 \\ / \\ C \\ \backslash \\ Sub^2 \end{array}$$

Form. VII.

wherein each of Sub^1 and Sub^2 is independently selected from the group consisting of hydrocarbyls having from 1 to 20 carbon atoms; silyl groups, amido groups and phosphido groups.

Cp is a ligand selected from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl and substituted fluorenyl; X is an activatable ligand and n is 1 or 2, depending upon the valence of M and the valence of X; and

M is a group 4 metal selected from the group consisting of titanium, hafnium and zirconium.

4. Process according to any on of claims 1 and 2, wherein 0 - 0.1 mol per mol of catalyst of further activating compound is used.

5. Process according to any on of claims 1 and 2, wherein no further activating compound is used.

6. Process according to any one of claims 1-5, wherein the catalyst used contains a phosphinimine ligand which is covalently bonded to the metal, defined by the formula:

$$\begin{array}{c} R^1 \\ \backslash \\ R^1 — P{=}N — \\ / \\ R^1 \end{array}$$

Form. VIII.

wherein each R^1 is independently selected from the group consisting of a hydrogen atom, a halogen atom, C_{1-20} hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical of the formula:

$$-Si-(R^2)_3$$ Form. IV.

wherein each R is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, and a germanyl radical of the formula:

$$-Ge-(R^{2'})_3$$ Form. V.

wherein $R^{2'}$ is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals.

7. Process according to claim 5, wherein the catalyst comprises as phosphinimine ligand tri-(tertiary butyl) phosphinimine.

8. Process according to any one of claims 1-6, wherein the alumoxane used is of the formula: $(R^4)_2AlO(R^4AlO)_mAl(R^4)_2$ wherein each R^4 is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and m is from 0 to 50.

9. Polymer obtainable by the process of any one of claims 1-7.

10. Polymer according to claim 8, wherein
[VNB] > 0.01 and
$\Delta\delta > 30 - 15$[VNB], provided that $\Delta\delta$ has no value below 0,
[VNB] is the content of vinyl norbornene in the polymer in weight % and
$\Delta\delta$ is, expressed in degrees, the difference between the loss angle δ at a frequency of 0.1 rad/s and the loss angle δ at a frequency of 100 rad/s, whereby the loss angle is calculated from the formulae $tg\delta = G''/G'$, whereby G' is the storage modulus and G" is the loss modulus, as measured by RDA, at a temperature of 125°C.

11. Polymer according to claim 9, wherein $\Delta\delta > 35 - 15$*[VNB].

12. Polymer according to any one of claims 8- 10, wherein the content of vinyl norbornene is between 0.1 and 4 weight %.

13. Polymer according to any one of claims 8-10, wherein the polymer comprises at least 0.01 weight % 5-ethylene-2-norbornene.

14. Polymer according to any one of claims 9 -13, wherein $\Delta\delta > 25 - 12{,}5.(Q^{-2})$, whereby Q = Mw/Mn, Mw is the weight average molecular weight and Mn is the number average molecular weight.

ABSTRACT

Process for the preparation of a polymer comprising monomeric units of ethylene, an α-olefin and a vinyl norbornene applying as a catalyst system:

a. a bridged or an unbridged group 4 metal containing catalyst having a single cyclopentadienyl ligand, a nitrogen containing ligand and at least one activatable ligand.

b. an aluminoxane activating compound,

c. 0 - 0.20 mol per mol of the catalyst of a further activating compound.

Preferably a bridged or unbridged catalyst is used according to formula:

```
Cp
 ¦  \
 ¦    M -Xn
 ¦  /
Z
```

wherein Cp is a ligand selected from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl and substituted fluorenyl;

X is an activatable ligand

Z is a nitrogen containing ligand

n is 1 or 2.